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<b>14. ABSTRACT</b>  <p>The Final Proceedings for Irish Atomistic Simulators Meeting 2000, 14 December 2000 - 15 December 2000</p> <p>The simulation of condensed matter at the atomic scale, using a range of current models and techniques. Both methodology and applications will be covered. The methodologies represented will be Quantum Monte Carlo, Classical Molecular Dynamics and Density Functional Theory (LDA/GGA) among others.</p>					
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**IAS2000**  
***5<sup>th</sup> Irish Atomistic Simulators'***  
***Conference***

**Department of Physics**  
**Queen's University Belfast**

***14-15 December 2000***



*A meeting of scientists in Ireland working on the fundamentals  
of atomistic simulation and its applications to materials,  
chemistry and other fields.*

**Adiabatic Internal Modes - A New Way to Gain Insights from Molecular Vibrational Spectroscopy;** *J. Andreas Larsson, NMRC, University College Cork*

Molecular vibrations are delocalized and involve all parts of the molecule. These constitute the normal mode vibrations which can be calculated with quantum mechanical methods, in the harmonic approximation. It is in general not possible to get information about localized quantities from normal mode vibrations. The Adiabatic Internal Modes which I will present, is a partitioning of the delocalized vibrations into the internal parameter space. Hence, it is now possible to get localized quantities from the vibrational spectrum. In my talk I will show how the adiabatic internal modes of a molecule can be used; a) for the interpretation of the vibrational spectrum; b) to calculate vibrational properties for internal parameters; c) to investigate the relationship between vibrational properties and geometrical properties, for chemical bonds.

**Calculation of the structure and dynamics of the Al<sub>2</sub>O<sub>3</sub> surface;** *Arnaud Marmier, Atomistic Simulation Group, Queen's University Belfast*

Alpha-alumina (Al<sub>2</sub>O<sub>3</sub>) has a vast range of technological applications, e.g. as a substrate in microelectronics or in catalyst technology. Nevertheless, despite extensive experimental and theoretical efforts, the structure of its (0001) surface is still not completely clear. Whereas most of the ab-initio calculations and many experiments identify an Al-terminated surface, some find that the surface is terminated by an oxygen plane. Some recent calculations have investigated the effects of the environment (Oxygen, Hydrogen, Water) on the stability of the different surfaces. We have chosen to study finite temperature effects by taking into account the surface lattice dynamics. The free energy of these surfaces is calculated within the quasi-harmonic approximation. The phonon dispersion curves are obtained using a supercell approach, in the framework of the local density approximation. We have also identified a surface mode of unusual amplitude, in agreement with the last tensor-LEED experiments.

**Tight-binding exploration of Alumina;** *Barbara Montanari, Atomistic Simulation Group, Queen's University Belfast*

Alumina (Al<sub>2</sub>O<sub>3</sub>) has at least eleven different polymorphs, the most stable of which is the corundum structure. The physical origin for the stability of this structure compared to others is still an open problem, and its solution involves a deeper understanding of the cohesive forces in alumina. A simple self-consistent tight-binding model is able to reproduce the electronic band structure and equilibrium lattice constant of the most stable structure, but it overestimates its bulk modulus. I will discuss the results of the inclusion of further effects in the model, such as the presence of electrostatic dipoles and quadrupoles, the non-orthogonality of the orbitals, and the electrostatic screening effect due to the spatial extension of the charge distribution.

**Localized Basis Quasiparticle Bandstructure Calculations;** *C.D. Hogan, M.D. Kuzmin and C.H. Patterson; Department of Physics, Trinity College, Dublin 2, Ireland*

It is well known that mean-field techniques (density-functional theory (DFT) and Hartree-Fock theory (HF)) tend to underestimate and overestimate, respectively, the band gap in many semiconductors and insulators. Consequently they are unsuitable for excited state calculations. A better description is given by the quasiparticle concept, which includes the effects of exchange and correlation via the self-energy operator [1]. Conventional methods for calculating quasiparticle bandstructures involve two main techniques, namely, the calculation of the self-energy within the GW approximation (GWA) as a correction to the DFT-LDA bandstructure and the use of a plane-wave basis set for constructing both the DFT-LDA bandstructure and the full dielectric matrix [2]. We present calculations of the quasiparticle bandstructure for NaCl and Si beginning with a Hartree-Fock Hamiltonian and a localized orbital basis. It is demonstrated that self-energy corrections reduce the grossly exaggerated Hartree-Fock band gaps significantly, although quantitative agreement with experiment is not achieved.

[1] L. Hedin, Phys. Rev. 139, A796 (1965)

[2] M.S. Hybertson and S.G. Louie, Phys. Rev. B 34, 5390 (1986)

**Diffusion in Strongly Inhomogeneous Systems;** *J.M. Don MacElroy, Department of Chemical Engineering, University College Dublin*

Current theoretical models for diffusion within inhomogeneous media are, paradoxically, largely based on pseudo-homogeneous mathematical analyses. While such an assumption may be reasonable in media containing 'homogeneous' domains which are large on a microscopic scale but small in macroscopic terms (e.g. mesoporous and macroporous media) this approach requires careful validation in its application to systems possessing strong structural (or energetic) inhomogeneities which extend over nanometer length scales. In this talk equilibrium and nonequilibrium molecular dynamics (MD) simulation results of two studies of self-diffusion of simple model fluids within nanopore structures are presented and discussed. In the first study non-equilibrium MD simulations of a Lennard-Jones fluid within a model crystalline pore are combined with the quasi-hydrodynamic theory of Pozhar and Gubbins (Phys.Rev., E56, 5367 (1997)) to demonstrate that the spatial dependence of the transport parameters should be taken into consideration to reliably predict the diffusion fluxes within zeolitic systems. The influence of the spatial dependence and, in particular, spatial non-locality, on the magnitude of the self-diffusivity is further demonstrated in the second study in which the results of both equilibrium and non-equilibrium MD simulations of single-file diffusion of a hard-sphere fluid in a simplified pore model are examined.

**Energy minimization for correlation terms in QMC wavefunctions;** *David Prendergast, Physics Department, University College Cork*

Parameterized correlated wavefunctions in quantum Monte Carlo (QMC) calculations are difficult to optimize in an automated fashion. Methods such as variance minimization require much human interaction and experience about the form of the wavefunction. We introduce an iterative method to optimize parameters in long-range (charge fluctuation dependent) correlation terms in Jastrow-Slater-type wavefunctions. This involves simultaneous optimization of approximately 1000 parameters to minimize the energy of the system. This is the first time that energy

minimization with respect to a large number of parameters has been shown to be stable in QMC.

**Accurate Calculations of Electronic Excitation Spectra with CI;** *Laura Tong, Andreas Larsson, Michael Nolan, T. Cheng and Jim Greer, NMRC, University College Cork*

MCCI is an efficient means of performing configuration interaction (CI) calculations, and has been applied to estimating full configuration interaction (FCI) and dissociation energies. We present a new study where the MCCI method is applied to the calculation of electronic excitations. A Monte Carlo generation procedure is used within the calculations for the expansion of the many-electron wavefunction, thus allowing for selection of configurations without bias to excitation level and without the explicit need for considering reference configurations. We have achieved what are to our knowledge the most accurate calculations of optical excitations for a wide variety of elements and spin couplings (singlet through quintet) with errors lower than 100 meV when averaged over states. If the high spin states are excluded, the average error between calculated and measured excitations reduces to typically 40 to 60 meV. To achieve these results, it is not necessary to extract 100% of the correlation energy for the ground and excited states, but rather to have a balanced treatment of the two states such that the energy differences yield accurate excitation energies. Several basis sets are explored for a description of the single particle functions and in analogy with correlation consistent basis sets, a set of rules for "excitation consistent" basis sets are derived.

**Exchange Coupling Mechanism in Manganites;** *M. Nicastrò and C.H. Patterson; Department of Physics, Trinity College, Dublin 2, Ireland*

The series of manganites  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  has been intensively studied in the last few years; their most important property is that they show colossal magnetoresistance in the doping range  $0.2 < x < 0.5$ . Unrestricted Hartree-Fock (UHF) total energy calculations on different spin structures are used to investigate the ground state properties of the parent compounds  $\text{CaMnO}_3$  and  $\text{LaMnO}_3$ . The calculated equilibrium geometry and the sign of the magnetic coupling exchange show agreement with experimental values. A number of theories have been proposed, mainly based on Anderson's superexchange, to explain what is responsible for determining the properties of these oxides. The superexchange mechanism and the role of configurations other than the ground state have been investigated using configuration interaction (CI) calculations on manganite clusters.

**Exchange Coupling Mechanism in Manganites;** *M. Nicastrò and C.H. Patterson; Department of Physics, Trinity College, Dublin 2, Ireland*

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**Photodissociation of Hydrogen Passivated Dopants in Gallium-Arsenide;** *Michael Nolan, Andreas Larsson, Laura Tong, Martin Murtagh, Jim Greer; NMRC, University College Cork*

There is a renewed interest in III-V technologies, notably gallium arsenide (GaAs), due to the explosion in mobile telecommunications and optical communications markets. GaAs heterojunction bipolar transistors (HBT) are a typical device used in the output amplifiers in mobile telephones. During epitaxial growth of the transistors, carbon is incorporated into the device by mixing carbon containing precursors into the growth chamber. The carbon dopants occupy arsenic sites on the lattice and thus act as p-type dopants. During processing of the devices, hydrogen present in the growth chamber can act to passivate the carbon dopants by the formation of C-H defects, thus reducing hole carrier concentrations and degrading device performance. Silicon doping can be introduced into GaAs where it occupies Ga sites and therefore acts as an n-type dopant, and a similar hydrogen passivation mechanism exists for the silicon doping. Photoenhanced dissociation can be induced for the Si-H bond leading to dopant re-activation, but this effect has not been observed for the C-H bond for photon energies up to 5 eV. The results of Monte Carlo CI calculations on the potential energy surfaces of the C-H and Si-H bonds in their respective ground and first excited triplet states are presented. The calculations predict that the C-H bond will not photo-dissociate for low photon energies in contrast to the Si-H bond.

**Distributed response analysis as a tool for molecular conduction and switching;** *Marc in het Panhuis; Materials Ireland Polymer Research Centre, Department of Physics, Trinity College Dublin, Ireland.*

Since its earliest days, molecular electronics has been concerned with electrical conduction, rectification and switching in single molecules. Much progress has now been made in studying these processes both experimentally and theoretically, and it is apparent that for a single molecule the perturbation caused by the electrical contacts is significant. Nevertheless, it is desirable to explore means of characterizing separately the propensity of molecules to conduct or switch. The distributed polarizability quantifies (among other things) the tendency for charge to flow between different regions of a molecule, which is analogous to conduction, while the distributed hyperpolarizability quantifies how the distributed polarizability depends on electric field, which is analogous to switching. In conjugated polyenes, studies of the effect of internal and external electric fields on bond length alternation have provided valuable insights into non-linear optics. Distributed response can be calculated rigorously for both linear and non-linear coefficients. Hence, although they characterize charge flow within rather than through molecules, distributed linear polarizability and quadratic hyperpolarizability appear suitable means to assess molecules as conductors and switches. Current silicon based electronic designs have fundamental limitations preventing reliable functioning on a nanometer scale. Molecular electronics can overcome these impediments, because it is possible (1x2)



**Reconstructions in White Paint;** *Simon Elliott, Dept of Chemistry, Trinity College Dublin*

Rutile is all around us, as the pigment in white paint - but there is more to it than that. As the focus in surface science shifts from metals to the more complex oxides, the (110) surface of rutile  $\text{TiO}_2$  has become a model system. While many experiments have confirmed the structure of the (1x1) rutile surface, controversy still rages over the (1x2) pattern. In our computational survey of possible (1x2) surface structures we hope to resolve this issue. The surface is modeled as a series of stacked slabs and electronic structure is calculated using First Principles DFT. A wide survey of (1x2) surface reconstructions is presented and the difficulties involved in estimating their surface energies are discussed. to construct single molecule devices, such as field effect transistors (FET). The distributed response can be used to identify superior switchable molecules for use in FET's.

**Dielectric Band Structure and Dielectric Response Eigenfunctions for fcc Argon;** *S. Galamiz-Mulaomerovic, C.D. Hogan and C. H. Patterson; Department of Physics, Trinity College Dublin*

Calculations of dielectric band structure and dielectric response functions for solid argon are presented. Using an approach similar to that of Baldereschi and Tosatti, the dielectric response function,  $R = \delta \rho / \delta V_{\text{ext}}$ , is expanded over a basis of eigenfunctions. The most important eigenfunctions of the response function and dielectric matrix are presented for argon and we demonstrate how they illustrate the multipolar nature of screening. A self-energy GW calculation of the band structure for solid argon is also presented. Wave functions are calculated within density-functional theory using the local-density approximation and a local orbital basis set.

**Quantum Monte Carlo Study of the Si(100) surface and its interaction with molecular hydrogen;** *Sorcha Healy, Department of Physics, National University of Ireland, Cork.*

The reconstruction of the Si(100) surface and its interaction with the hydrogen molecule poses several interesting questions. STM and other experimental techniques have predominantly shown the Si(100) surface to consist of rows of alternating buckled dimers. Density Functional Theory (DFT) calculations on slab geometries do predict this reconstruction, while highly correlated quantum chemistry (QC) methods on small model clusters favour a symmetric configuration. We investigate the reconstruction using Quantum Monte Carlo (QMC) methods on large clusters. The interaction of  $\text{H}_2$  with the Si(100) surface is another long-standing issue. The process follows first order kinetics, which puts a constraint on the possible mechanisms. Although desorption experiments have found no substantial adsorption barrier, the sticking coefficient of  $\text{H}_2$  on Si(100) is found to be very small, in apparent violation of detailed balance. DFT calculations on slab geometries and correlated QC calculations on small clusters lead to completely different mechanisms, each with limited agreement with experiment. Again we use QMC methods to compute accurate adsorption/ desorption barriers. We show that the mechanism preferred by slab-DFT, does not explain the experimental findings: the agreement between DFT calculations and experiments on the desorption barrier was fortuitous and simply due to the use of approximate exchange-correlation DFT functionals.

Collaborators: C Filippi (NUI, Cork), P. Kratzer and M. Scheffler (Fritz-Haber Institut, Berlin), E. Pehlke (University of Essen).

**A comparison of continuum and explicitly molecular models for the description of small organic molecules in aqueous solution;** *Stuart Murdock, Atomistic Simulation Group, Queen's University Belfast*

A simple model to represent solvating water is to describe the solvent as a dielectric continuum and treat the system using electrostatics. An improvement would be to add some discontinuity to the continuum that account's for interaction of solvent molecules close to the solute. A further improvement would be to use explicitly molecular models where each solvent molecule is individually represented. *ab initio* methods could be used instead of classical methods. There are wide varieties and styles of calculations/ models that can be used. How good a model is needed to describe the nature of each equilibrium properly? Conformational and tautomeric equilibria in aqueous solution are described by continuum and explicitly molecular methods and the differences are discussed in terms of energetics and solvation structure.

**A model for the simple estimation of reaction barriers in heterogeneous Catalysis;** *Zhipan Liu and Peijun Hu; School of Chemistry, Queen's University Belfast*

It is well known that catalytic, particularly, heterogeneous catalytic reactions play an important role in many processes. To date, however, the catalysts are by and large developed by trial-and-error methods. Obviously a catalyst preparation by design is highly desirable. It has long been realized that the designing of catalysts may be achieved if catalytic reaction barriers can be predicted, because macroscopic reaction rates depend exponentially on the reaction barriers. In particular, estimation without heavy calculation would be especially useful to instruct experiments. Therefore to understand catalytic reaction barriers and ultimately to be capable of the simple estimation of the reaction barriers is one of the biggest goals in chemistry. Despite tremendous efforts in the last few decades, it has little success due to the volatile feature of reaction barriers, varying from zero to several electron volts. Here we have systematically studied several typical heterogeneous catalytic reactions on several important transition metal surfaces, using density function theory (DFT). By detailed analyses, we have obtained a model, which, we believe, is a step towards this seemingly insurmountable goal.